

Penetration-Sorption of Cotton Fibers Measured by Immersed Weight

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Synopsis

Weight of cotton immersed in an aqueous solution (various concentrations of NaOH) was explored as a basis for assessing penetration and sorption of the solute. The overall effects of swelling are indicated. Penetration and sorption phenomena can be identified with supplementary information, but they cannot yet be quantified. This methodology supplements and complements gel filtration as a means of measuring interactions between solutes in aqueous solution and cellulose fibers.

INTRODUCTION

Accessibility, swelling, permeation, and penetration have been measured by numerous methods.¹⁻⁴ However, these methods are not generally applicable to the solutes in aqueous solutions used in conventional or experimental finishing of cotton. Studies involving gel filtration of aqueous solutions of solutes through columns of cotton cellulose have shown that penetration is a function of molecular size, that exclusion is a function of bound water in cotton, and that sorption is a function of the structure of the reagent molecule.^{5,6} However, additional methodology is needed for assessing penetration, exclusion, and sorption to supplement and complement the gel filtration method.

Density, specific gravity, or specific volume of cotton fibers and other porous substrates measured by the displacement of liquids varies with the immersion medium. The variation is generally attributed to different degrees of accessibility of the liquids to the total potential pore structure. It has also been interpreted in terms of compression of liquid in the film on the surface of pores under the action of attractive forces.⁷ Fortess⁸ used a pycnometer displacement method to measure the specific gravity of cellulose acetate yarn in various organic liquids and, thereby, to study the rate and extent of penetration of these liquids. In such studies, a low value for specific gravity or a high value for specific volume indicates little or no penetration. A high value of specific gravity indicates penetration below the surface of the fiber.

We were interested in evaluating density or specific gravity measurements of cotton fibers to assess penetration and sorption. We examined aqueous NaOH as the penetrant because pertinent information from swelling measurements was already available for such solutions. We describe here the results obtained by weighing cotton and mercerized cotton fabric while immersed in solutions of various concentrations of NaOH. The same principle—volume displacement—is involved whether the results are discussed in terms of effective weight, density, or specific gravity.

EXPERIMENTAL

Materials

The cotton was desized, scoured, bleached cheesecloth. Mercerized cotton was prepared by immersing cheesecloth without tension in 16% (w/w) NaOH at room temperature for 30 min and rinsing in water, 5% acetic acid, and finally water.

Methods

Effective Immersed Weight per Gram of Cotton

Apparatus. A glass container $7.2 \times 7.2 \times 9.0$ cm with flat sides was placed upright on a glass platform bridging the pan of an analytical balance. A platinum wire was fixed to the hook at the top of the balance pan and the other end was attached to a miniature stainless-steel clamp to be located just beneath the surface of liquid in the glass container.

Procedure. The immersion medium was placed in the glass container, and the effective weight of the platinum wire clamp system (W_c) was obtained. Duplicate samples of cotton that weighed 1.0 g in air were dried for 1 hr at 105°C. The dried weights (W_d) were obtained, and the samples were placed in the immersion medium. After extensive equilibration (overnight) to allow completion of penetration and sorption and elimination of bubbles on the fibers, the samples were suspended by the clamp one at a time. Total effective weights (W_t) at 25°C were measured to 0.1 mg. Effective weight per gram of cotton (W_e) is equal to $(W_t - W_c)/W_d$. The average difference between duplicates was 1 mg. This method is essentially that of Hermans^{9a} for the determination of density in water.

The density of each immersion medium was determined at 25°C to four decimal places by a 2-ml pycnometer.

RESULTS

Effective weights (W_e) of desized, scoured, bleached (DSB) cotton fabric and mercerized cotton fabric (both in the form of loose woven fabric) as a function of densities of NaOH solutions are summarized in Figure 1. For NaOH solutions with densities below about 1.15 g/cm³ (below 14% NaOH), which is borderline for complete mercerization at 25°C,¹⁰ DSB and mercerized cottons exhibited significantly different W_e . Above solution densities of 1.15 g/cm³, the data points for the two cottons were indistinguishable.

The origin of the dashed line in the primary portion of Figure 1 is shown in the miniature plot. This line extends from the point (*) on the ordinate representing the weight of the sample theoretically measured in vacuum, but actually in air, to the point (×) representing the weight of the sample immersed in water to the point (Δ) of intercept with the abscissa. The last point constitutes an estimate of the density of liquid in which the cotton fibers neither float nor sink. Point Δ is, therefore, an estimate of the apparent density of the microstructure of cotton cellulose in which the pores have been permeated with water. In Figure 1, point × is the same for DSB cotton and mercerized cotton.

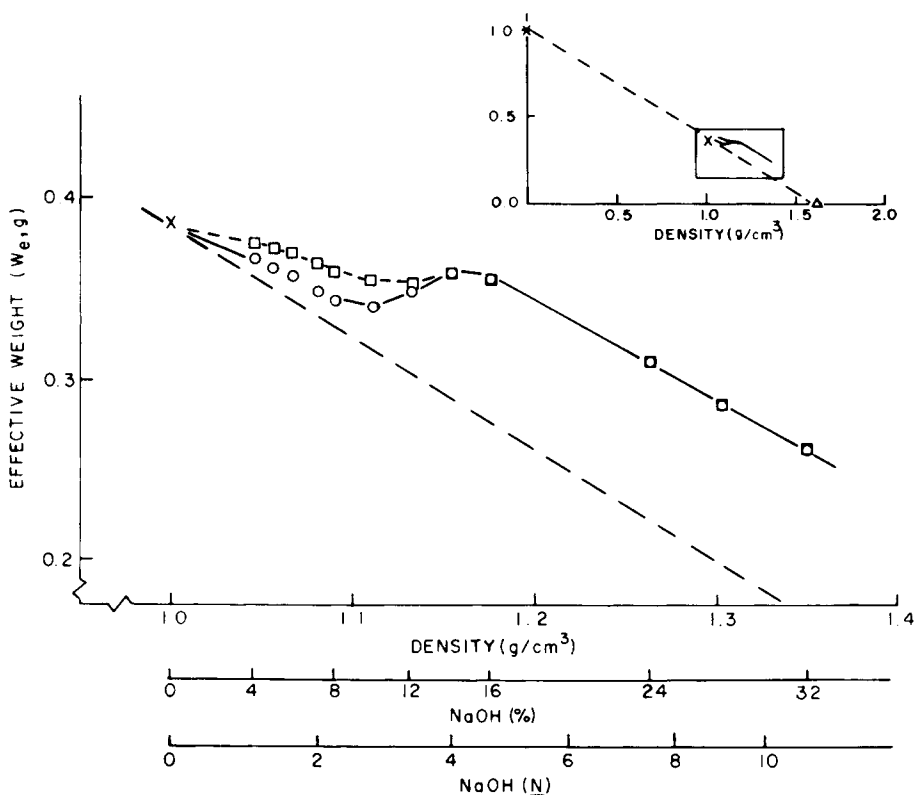


Fig. 1. Effective weight of cotton as a function of the density of the medium (or weight concentration or normality of NaOH) in which the cotton was immersed. Symbols designate weighings as follows: (*) in air, (X) in water, (O) native cotton in various solutions of NaOH, (□) premercerized cotton in solutions of NaOH, (Δ) extrapolated value denoting the density of a solution in which the cotton would neither sink nor float. The miniature plot at upper right shows the origin of the dashed line and provides perspective for the plot in the main portion of the figure.

DISCUSSION

The W_e of a porous solid in a pure liquid is a function of (1) the density of the liquid, (2) the ability of the liquid to penetrate pores, and (3) the degree of sorption of liquid on pore surfaces. Background information is summarized by Hermans^{9b} and Fahmy and Mobarak.¹¹ For the cellulose-water system, networks of channels and pores do not exist in the dry fibers but are opened up from submicroscopic and subelectron microscopic imperfections in lateral packing on exposure to water.¹² Water is the best liquid penetrant, as indicated by densities of purified cellulose from liquid displacement: about 1.55 g/cm³ for several organic liquids,^{9b} 1.62 for water,¹¹ and 1.63 (ref. 12) calculated from dimensions of the unit cell of cellulose. In this case with a commercial cotton fabric, the apparent density represented by the intercept of the abscissa (Δ) in the miniature plot in Figure 1 was 1.60 g/cm³.

Part of the water within a moist cellulosic substrate exhibits properties different from those of the bulk water, because it is bound to or strongly perturbed by cellulosic surfaces.¹³ The amount of such water is unresolved,¹³ and it is not clear that it contributes to the W_e as noted in function (3) above; for these reasons and for that in the following paragraph, we set the question aside. The effects

of increasing the factors 1–3 noted above are (1) to decrease W_e , (2) to increase W_e , and (3) to increase W_e , respectively.

To first approximation, W_e of a porous solid in a solution depends upon the factors noted above (liquid density, penetration, and sorption). The situation, however, is complicated in at least two ways by the presence of the solute: (1) the solute molecule, being different in molecular size from the solvent molecule, may be excluded to a greater or lesser extent, and (2) the solute may undergo sorption on cellulosic surfaces. Both of these phenomena have been observed.^{5,6}

In the cellulose–water system, common solute molecules are always larger than the water molecule and depend upon the latter to open up the pore system. Thus, the solute cannot penetrate into pores below a limit that is characteristic for each solute. The smaller pores will accommodate only water. The solute can interact with and sorb onto cellulosic surfaces to an extent that is greater or lesser than that of water. The effects of selective exclusion of the solute from small pores and of selective sorption of the solute on surfaces are, respectively, to reduce W_e and to increase W_e . The reduction in W_e occurs because water in the smaller pores generally has a lower density than the solution and therefore provides a buoyancy. On the other hand, sorption increases weight by appending solute molecules onto cellulosic surfaces.

In Figure 1 the dashed lines in both plots constitute baselines against which penetration and sorption of NaOH solutions into native and premercerized cottons may be assessed. Points above the baseline indicate increased penetration and/or sorption relative to water; those below the line indicate exclusion of the solute.

With these points in mind, it is appropriate to examine the experimental data in Figure 1 in some detail.

General Measure of Swelling

The higher W_e for mercerized versus DSB cotton indicates increased penetration and/or sorption. This behavior is consistent with the greater accessibility¹⁴ and greater internal pore volume¹⁵ measured for mercerized cotton. The convergence of curves for the two cottons in NaOH of density about 1.15 g/cm³ and above is expected but verifies that the final states of penetration and sorption are the same in both cases.

Data of Warwicker^{16,17} obtained from changes in the widths of native fibers in various normalities of NaOH provide a basis for comparing our results. Our data in Figure 1 and Warwicker's data¹⁷ were normalized to the same scale in Figure 2. This normalization is arbitrary. The swelling of the cotton fiber in water is set at zero and that of the DSB cotton fabric in 4.0*N* NaOH is set at 1.0 for each set of data. The critical dimension for transposing data from Figure 1 is the vertical distance between experimental points and the base line. The more useful portions of the plots in Figure 2 lie between zero and 4.0*N* NaOH. For both curves, the steepest portions of the curves lie in the 2–4*N* range. Lattice conversion occurs in this range. In Warwicker's study¹⁶ lattice conversion began in 3*N* NaOH.

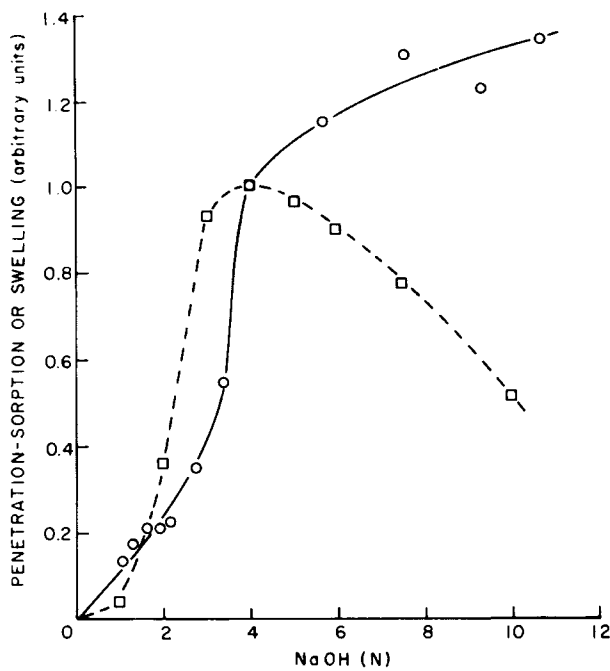


Fig. 2. Extent of penetration-sorption (O and solid curve) or extent of width swelling (□ and dashed curve) of cotton at 25°C as a function of normality of sodium hydroxide solutions. Penetration-sorption data are from Figure 1 and width swelling data are from Warwicker (ref. 17). Both of these curves are normalized so that the value on the ordinate is zero for native cotton in water and is 1.0 in 4.0*N* NaOH.

Penetration

Warwicker noted substantial width swelling of the cotton fiber in 2*N* NaOH and attributed it to interfibrillar swelling because no lattice change occurred up to this point. Similarly, in our measurements the increase in W_e up to and somewhat beyond 2*N* NaOH must represent, at least in part, an increase in penetration between microfibrillar units with an increase in concentration of NaOH. This conclusion is substantiated by observations in which samples of cotton subjected to swelling in 0.1, 0.5, 1.0, 2.0, and 4.0*N* NaOH exhibited a gradual increase in water imbibition.¹⁸ Thus, internal volume and surface in the cotton fiber are increased by penetration of base before lattice change occurs.

The steep increase in W_e in the 3–4*N* range must result primarily from penetration of solution into the crystalline lattice.

Sorption

In gel filtration measurements involving cellulose and Sephadex (as a model for cellulose), hydrogen bonding sorption was identified for amides (in proportion to protons on the N), and strong sorption was observed in the case of amines.⁵ In the current study, we observed that W_e of cotton in neat ethylenediamine (density = 0.9076) fell above the baseline shown in Figure 1 (by ~0.035 units). This same agent is sorbed onto cotton surfaces in dilute aqueous solutions. This

type of strong interaction is probably a prerequisite for a decrystallizing agent (ethylenediamine, sodium hydroxide, etc.).

More specific evidence concerning sorption of NaOH lies in the formation of adducts of NaOH at the O(2)H and O(3)H of methyl glucoside¹⁹ or cotton cellulose.²⁰ This adduct formation, which represents a type of sorption, increased with increasing concentration of NaOH. Thus, the increase in W_e for cotton in NaOH above 4*N* (Fig. 2) may be attributed entirely to increasing sorption of NaOH. This same type of sorption may occur over the entire range of concentrations of NaOH and simply be imposed on top of the effect from penetration.

CONCLUSIONS

The method and technique reported here provide means of assessing the composite of penetration-sorption of strong swelling agents for cotton cellulose. No simple means of estimating penetration and sorption individually is presently available. Data obtained by this method supplement those from gel filtration. It appears that useful information on exclusion of solutes in aqueous media from pores of cotton may be obtained by this method.

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